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Chemical Sensors from Carbon Nanotubes

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Introduction: There exists a clear need in the Department of Defense for small, sensitive, and rapid-response sensors of dangerous chemicals and explosives. To address this need, we are developing devices based on random networks of single-walled carbon nanotubes (SWNTs).¹ The carbon nanotube, a carbon phase that can be described as a hollow tube one nanometer in diameter, one atom thick, and several microns long, is very nearly an ideal material for sensor applications: it is highly nonreactive while at the same time all of the electronically active area is at the surface. We have found that SWNT network-based transducers rapidly and reversibly respond to a wide spectrum of dilute chemical vapors. We are working with colleagues in the Materials Science and Technology Division to improve the specificity of the devices and to turn this novel transducer design into a fieldable and useful sensor technology.

Carbon nanotubes were initially discovered about a dozen years ago. Demonstration of sensitivity of single nanotube conductance to ambient species was only six years ago. However, such single nanotube devices are difficult and expensive to fabricate. A key innovation of our laboratory is the use of networks of randomly grown nanotubes as the active sensor material.² Such SWNT network sensors can be fabricated with high yield by using conventional microfabrication technology (Fig. 4). Additionally, the use of SWNT networks dramatically reduces the level of $1/f$ noise, a critical factor for sensor applications, but an intrinsic feature of nanoscale electronic materials.

Transducer Physics: We test the transducer by blowing dilute concentrations of vapor in air from various liquids and solids across the active area and monitoring the capacitance C between the network and the substrate as well as the conductance G across

the network.³ We observe a C and G response to nearly all analytes tested, and further that these responses increase monotonically and smoothly with concentration over a wide range (Fig. 5). Further study has revealed that the dominant physical mechanism behind sensitivity to ambient is adsorption of species on the surface of the nanotubes. Surface coverage by adsorbed species is related not to the concentration of species in the ambient (i.e., the partial pressure P), but rather to the fraction of the equilibrium vapor pressure P/P_0 . In other words, our transducer responds to analytes not according to their local abundance (P) but according to their likelihood of condensing on a surface (P/P_0). As a result, our sensor responds equally well to both high and low vapor pressure materials. Since the low vapor pressure of many materials of interest, such as nerve agents, blister agents, and explosives, has made their detection by conventional sensors a challenge, this indicates an area where our sensor offers unique capabilities. Furthermore, equilibrium between surface adsorbates and ambient is rapidly established, implying subsecond response times (which we observe).

Changes in C are primarily associated with the intrinsic dipole moment of the analyte. Changes in G are primarily due to charge transfer interactions between the analyte and the nanotube. The ratio of these two terms is a constant for a given analyte, and can be used to distinguish even closely related species. In Fig. 6, we show that the response of the transducer to doses of $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CH}_3$, a simulant for a nerve agent, and structurally similar $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$, produces two distinct C to G ratios. Thus, the transducer can be used to match a response to a library of values from known materials.

In an effort to increase both sensitivity and specificity, we have modified our devices by applying thin films of certain sorbent polymers or self-assembled monolayers. Many of these materials were developed by the NRL Materials Science and Technology Division for use in surface acoustic wave sensors, and are known to be highly efficient and selective concentrators of materials out of vapor phase. Work in this area is ongoing.

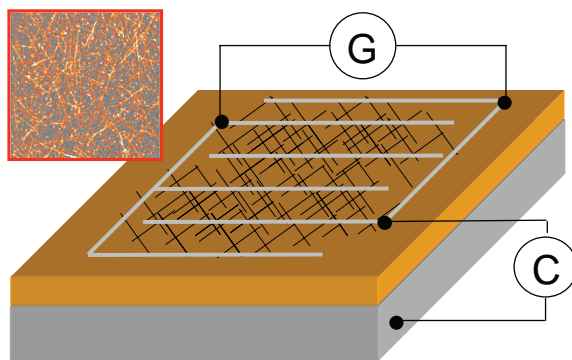


FIGURE 4
Schematic of transducer design and measurement configuration, with an atomic force microscope (AFM) image of the SWNT network shown as an inset. The tubes are about 1 nm in diameter.

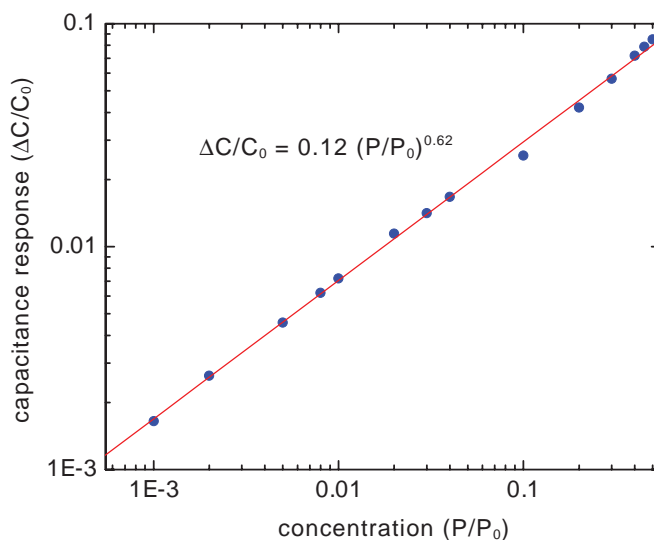


FIGURE 5

Measurements of transducer capacitance response $\Delta C/C_0$ vs fraction of equilibrium vapor pressure for acetone, along with a best fit for a power-law relationship. Our noise floor for $\Delta C/C_0$ is conservatively established as 10^{-4} . This implies a minimum detectable level of $P/P_0 = 1 \times 10^{-5}$ for this material.

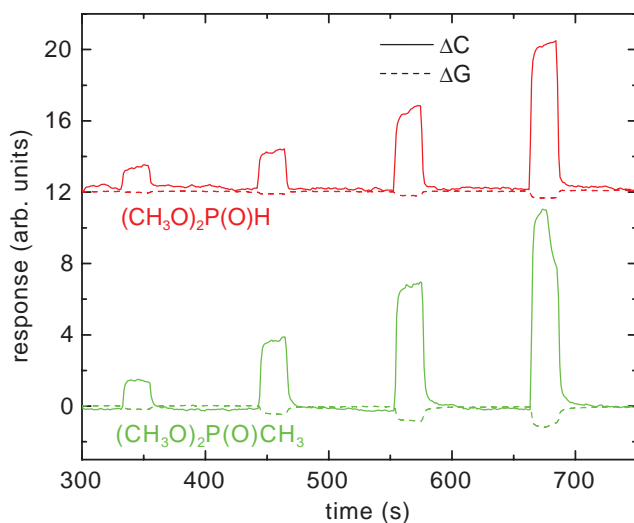


FIGURE 6

Capacitance C and conductance G responses at four different concentrations for two similar materials. The ratio of C and G is constant over the concentrations shown, but different for the two materials: -0.04 for DMPH and -0.12 for DMMP, after appropriate normalizations.

Summary: We have found these devices to be rapid and sensitive transducers of chemical exposure, generally exceeding performance of existing commercial devices meeting the same application niche. They are easy to manufacture in large quantities. Strategies are in hand to increase discrimination of agents. Integration with existing sensor units is currently under development, in collaboration with the Materials Science and Technology Division.

- ¹ E.S. Snow, F.K. Perkins, E.J. Houser, S.C. Badescu, and T.L. Reinecke, "Chemical Detection with a Single-Walled Carbon Nanotube Capacitor," *Science* **307**(5717), 1942-1944 (2005).
- ² E.S. Snow, J.P. Novak, and P.M. Campbell, "Interconnected Networks of Single-Walled Carbon Nanotubes" U.S. Patent No. 6,918,284.
- ³ E.S. Snow and F.K. Perkins, "Capacitance and Conductance of Single-Walled Carbon Nanotubes in the Presence of Chemical Vapors," *Nano Letters* **5**(12), 2414-2417 (2005). ★

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